

SEPARATION OF GAS MIXTURES BY TRANSITION-METAL COMPLEXES

M. A. Lilga, R. T. Hallen, D. A. Nelson

Battelle, Pacific Northwest Laboratory
P.O. Box 999
Richland, WA 99352

INTRODUCTION

The selective separation or purification of gases, especially hydrogen and CO, is highly desirable in processes utilizing product gas from coal gasification. However, gas separation is a difficult and energy intensive process. The development of new and innovative methodologies to selectively and efficiently separate specific gas components from mixed-gas streams would significantly reduce the cost and complexity of product gas production and processing. For example, efficient H₂ separation from synthesis gas could make coal an attractive future source of H₂ for use as a fuel or chemical feedstock. In addition, this technology could have a significant impact on processes not directly associated with coal gasification in which hydrogen is lost in a waste stream. These processes include ammonia manufacture, reduction of metallic oxide ores, and hydrogenation of fats and oils. Thus, wide-ranging applications exist for hydrogen separation and recovery technologies.

Current separation technologies are inefficient or non-selective. For example, recovery of H₂ from Pressure Swing Adsorption is on the order of 80%. PSA is ineffective with feeds containing less than 50% H₂. The COSORBTM process for CO recovery is highly moisture sensitive, requiring removal of water from feed streams. Membranes are inherently energy efficient but systems, such as PRISMTM, cannot separate H₂ from CO₂.

The Pacific Northwest Laboratory (PNL) is examining transition-metal complexes as selective agents for the separation of syngas components from gas mixtures. Transition-metal complexes are known which react reversibly with gases such as H₂, CO, O₂, and CO₂. This reversible binding can be used to transfer the gas from a region of high partial pressure to a region of lower partial pressure. The selectivity of transfer is determined primarily by the selectivity of the metal in binding a specific gas. The nature of the ligands surrounding the metal has a large influence on the selectivity and reversibility and we have successfully used ligand modification to prepare complexes that have improved properties for H₂ or CO binding. Applications of metal complexes to gas separation and two specific examples of metal complexes under study will be discussed.

APPLICATION OF METAL COMPLEXES TO GAS SEPARATION

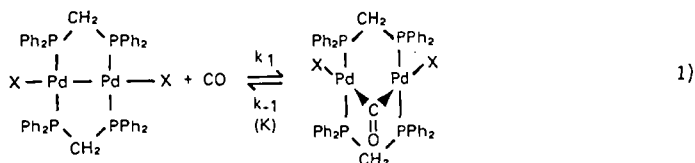
Two gas separation systems which take advantage of selective, reversible gas binding by transition-metal complexes are absorption/desorption and facilitated transport membrane systems. A two-column apparatus used at PNL is shown in Figure 1 and its operation is illustrated for CO separation. Inlet gas containing CO enters the bottom of the absorber column and encounters a counter-current flow of solution containing a metal complex. Non-reactive feed gases exit the top of the absorber while CO is transported to the stripper column in the form of a CO/metal complex. Heat and an inert stripping gas release the CO from the metal complex in the stripper column. CO product gas exits the top of the stripper column and volatilized solvent is condensed and returned to the system. The solution containing regenerated metal complex is recycled to the top of the absorber column, and the cycle begins again. This apparatus is similar to that used in the COSORBTM process and allows for continuous gas separation. Any gas could be separated from a feed stream by this process assuming an appropriate metal complex/solvent system

specific for that gas is available. Potential drawbacks include the relatively large amounts of carrier required and the interference of solubility of undesired gases in the solvent.

Immobilized liquid membrane systems, in which the metal complex acts as a facilitated transport agent, offer the potential for high selectivity and increased flux. This type of system is illustrated in Figure 2 for H_2 separation. The driving force to separation is a pressure gradient across the membrane. Hydrogen entering the membrane on the high pressure side reacts with a metal complex. The metal/hydrogen complex diffuses across the membrane where H_2 is released in the H_2 -lean environment and product H_2 leaves the membrane and is removed. A concentration gradient drives the metal complex back across the membrane and more H_2 is bound to continue the cycle. The function of the metal complex is to act as a specific carrier for H_2 and serves to increase the effective H_2 concentration in the membrane relative to the undesired gases. Thus, selectivity for H_2 is high, allowing the use of thinner membranes resulting in a greater flux. Permeability and selectivity in these systems are expected to be significantly greater than for dry or liquid-wetted membranes.

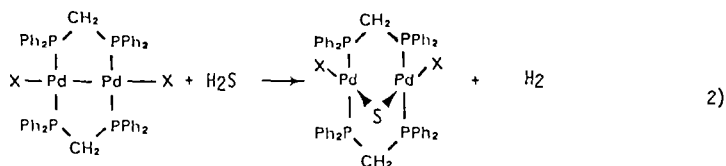
PALLADIUM COMPLEXES

Palladium dimer complexes were evaluated for their ability to reversibly bind CO (Equation 1). Kinetic and thermodynamic data for these complexes ($X = NCO, Cl,$



Br, I) indicate that halide substitution greatly influences the binding of CO (1). For example, the equilibrium constant, K , for CO binding follows the order $NCO > Cl > Br > I$ where K for the NCO complex is approximately 300 times that of the iodide complex. This difference in equilibrium constant is primarily due to differences in k_{-1} , the rate of CO dissociation.

Specificity for CO is high. Gases including CO_2 , N_2 , H_2 , O_2 and ethylene do not interfere with CO binding. H_2S was found to react in a novel way to release H_2 according to Equation 2 (2).

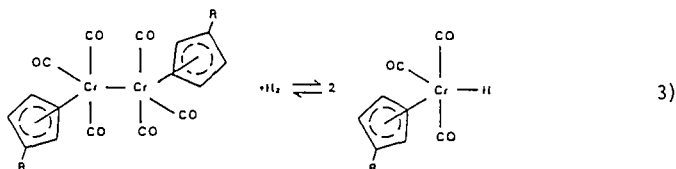


Equilibrium data for the bromide complex indicated suitable reversibility over the temperature and CO pressure ranges of interest. This complex was chosen for

bench-scale experiments in the absorber/stripper system shown in Figure 1 (3). Presence of the complex enhances transfer of CO by an order of magnitude and the system functions to separate CO from N₂. With a five-component mixture (CO, CO₂, H₂, CH₄, and N₂) a combination of chemical complexation of CO and the solubility of CO₂ and CH₄ in the solvent resulted in significant transfer of these gases to the stripper. Little H₂ was transferred and an H₂-rich gas stream was produced indicating the potential of this system for H₂ separation from a low-btu gas mixture. A cost analysis indicated that the initial costs of palladium were not necessarily prohibitive but to compete with existing technology the lifetime of the complex must be at least one year.

CHROMIUM COMPLEXES

The reaction of H₂ with [CpCr(CO)₃]₂ (Cp = cyclopentadienyl, C₅H₅) was reported by Fischer, et al. (4,5) to occur at 70°C and 150 atm H₂ to afford the monomeric hydride complex CpCr(CO)₃H. It has also been reported that the pure monomeric hydride complex evolves H₂ when heated to 80°C, its melting point. Our initial objective was to determine the temperature and H₂ pressure conditions required to carry out the reversible H₂ binding in solution (Equation 3).



Derivatives of the complex were also prepared to study the effects of electron-withdrawing groups on the cyclopentadienyl ligand (R = CO₂CH₃) on Equation 3. Our investigation has demonstrated that the reaction of H₂ with [CpCr(CO)₃]₂ is much more facile than previously reported. At 10 atm and room temperature, the reaction is complete before a spectrum can be taken. This dimer is found to react with 1 atm H₂ slowly at room temperature but faster at 65°C, reaching completion in 0.5 hours. Regeneration to the extent of about 5% can be achieved by heating to 100°C for 2 hours. H₂ is rapidly lost upon photolysis, however, CO is also lost and an inactive complex is formed. The substituted complex shows similar activity for H₂ binding but regeneration appeared to be easier with 10% conversion at 90°C after two hours. Regeneration may be difficult because it involves a bimolecular process in which two chromium centers interact. It is possible that regeneration will be improved by linking the cyclopentadienyl groups together, since hydrogen formation would then be unimolecular.

CONCLUSIONS

Selective transition-metal complexes can enhance gas transport in gas separation processes. Properties of complexes can be tailored by chemical modification of the ligand environment to improve binding characteristics. As a result, high selectivity for specific gas components is attainable. In addition, complexes need not be prohibitively expensive.

ACKNOWLEDGMENT

This research was supported by the U.S. Department of Energy, Morgantown Energy Technology Center under contract DE-AC06-76RLO 1830.

REFERENCES

- (1) Lee, C. L.; James, B. R.; Nelson, D. A.; Hallen, R. T. *Organometallics*, 1984, 3, 1360.
- (2) James, B. R.; Lee, C. L.; Lilga, M. A.; Nelson, D. A. U.S. Patent 4 693 875, 1987.
- (3) Lyke, S. E.; Lilga, M. A.; Ozanich, R. M.; Nelson, D. A. *Ind. Eng. Chem. Prod. Res. Dev.*, 1986, 25, 517.
- (4) Fischer, E. O. *Inorg. Synth.*, 1963, 7, 136.
- (5) Fischer, E. O.; Hafner, W.; Stahl, H. O. *Z. Anorg. Allgem. Chem.*, 1955, 282, 47.

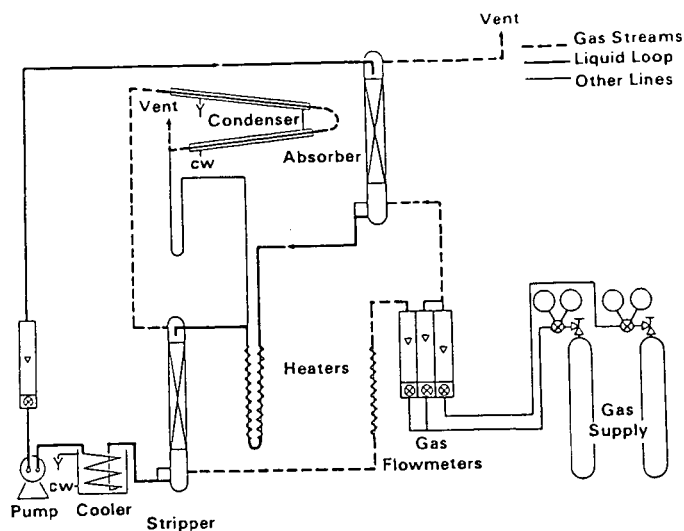


FIGURE 1. Absorber/Stripper Apparatus

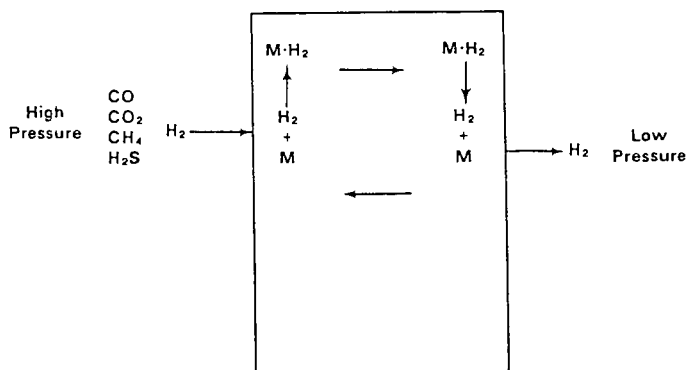


FIGURE 2. Facilitated Transport of H_2 by a Membrane Containing a Dissolved Metal Complex